Introduction

Since its discovery by explorers in the 1800s, the Western United States has had a long history of natural resource extraction. What began with the gold and silver rushes has developed into a clamoring for energy development and use that continues with relentless force. Coal, oil, and natural gas have become a sort of new gold of the West. Much like the first years of mining, natural resource extraction remains a volatile undertaking. While the nation's demand for energy typically increases with expanding populations, the fluctuating prices of oil and gas can lead to massive boom-and-bust economic cycles that leave towns devastated who depend on the industry for their livelihood.

Natural gas, a viable energy source that has become increasingly utilized in the last several decades, has experienced such cycles on perhaps a greater level than even coal or crude oil. However, its status as a "transition fuel" to a new energy economy has presently brought it to the forefront of American energy development. Natural gas currently produces 16 percent of the electricity in the United States; and energy is also its fastest growing use. It is likely that it will remain indispensible in our energy portfolio for years to come because of its plethora of uses in heating, cooking, and recently, fueling vehicles. Of the three main fossil fuels, it is the most efficient and cleanest-burning (Bryner, 2003).

But is natural gas really as clean as energy developers and the industry claim? Despite the decrease in natural gas activity in recent years with a struggling economy and declining market value, concerns about the impacts of drilling and extraction to the environment and public health remain. Several of the processes involved in these activities generate the potential for contaminants to be released; and determining their exact effects will continue to be a prevalent field of research and study. A process called hydraulic fracturing, also known as "fracking," involves the use of millions of gallons of water, sand, and chemicals injected into tightly-packed geologic formations to stimulate the flow of natural gas toward the producing well. While the industry asserts that there is little movement of these fluids away from their target formation, other evidence suggests that fracking fluids can not only migrate into adjoining formations but also cause the flow of potentially toxic hydrocarbons towards the earth's surface.

Of course, it should be essential during natural gas development to protect one resource we all cannot live without: water. There are numerous ways in which natural gas extraction can impact water quality (and quantity, for that matter), such as utilizing potentially harmful chemicals in drilling and hydraulic fracturing activities that can run or seep into surface and groundwater. Produced water extracted along with natural gas can also contain carcinogenic compounds, as well as toxic metals and metalloids (Ryan, 2009).

In recent years, new technologies have allowed for extraction of natural gas reserves that were previously impossible, causing a large expansion of the natural gas industry all over the west. Western Colorado, containing reserves of several unconventional sources, has seen expansion of the industry nearly equal that of other regions but has produced relatively little scientific literature about the subject. Many local environmental groups and other organizations believe that several of the processes involved in natural gas extraction there could be negatively affecting public health.

Concerned citizens and stakeholders are speaking out in frustration about what they believe is negligence on the part of the industry in maintaining environmental quality and preventing contamination. While natural gas is a viable energy source that should be explored and utilized, this study hypothesizes that drilling and extraction processes may generate wastewater that is present in concentrations that could be harmful to surface and groundwater quality. We will seek to better understand these impacts and determine if they do in fact present a serious problem to regions experiencing serious natural gas activity.

There are varying but significant impacts to water quality in natural-gas producing regions. Local geology influences the amounts of water each formation contains, the types and concentrations of various contaminants, and the extent of hydraulic fracturing that may be used. The impacts of drilling and extraction, despite numerous studies in the last several decades, are still largely unknown. Regions all over Western Colorado have seen high levels of natural gas development in recent years, including the Fruitland Outcrop in the San Juan Basin of southwestern Colorado, the Uinta Basin of northwestern Colorado and northeastern Utah, and the Piceance Basin in central western Colorado. The Piceance Basin has been a hotbed of debate between local landowners and the industry, producing questions of whether contaminants released in their drilling and extraction processes have the potential to migrate into residential wells and surface tributaries. Because the Piceance Basin and specifically Garfield County have been under-represented in the scientific literature, we will seek to explore how natural gas extraction may be affecting water supplies in these areas.

Background

Before describing our experimental process and results, it is helpful to understand the depth of the issue of natural gas development in the west. We will first explore the geologic sources of natural gas to indicate factors contributing to industry presence in certain regions and the practices they use. Next we will examine the various impacts to water quality that may result from natural gas activity and the contaminants associated with them. Finally, the location of our research will be described in depth along with the adverse health impacts that many believe they have experienced there.

Geologic Sources of Natural Gas

In the initial years of natural gas extraction, technological limitations only allowed for the extraction of conventional natural gas, which is found largely in formations like sands and carbonates. This gas is held in interconnected rock pores that allow for easy flow to the wellhead (DOE, 2009). Development is typically much slower, and often only one well can be drilled from a well pad. However, the increased demand for natural gas in the U.S. energy supply has led us on a search for more economically viable, efficient, and productive sources. New technologies such as directional drilling have allowed operators to drill as many as 24 wells from a single pad, reducing the terrestrial impacts of development.

These improvements in technology have facilitated expansion of the industry into diverse regions of the nation, allowing extraction from previously untouched reservoirs of natural gas. Termed "unconventional sources," they now constitute the majority of the market. These are produced mainly from tightly packed formations that often require stimulation of new pore spaces to allow gas flow to the surface, typically by a process called hydraulic fracturing. There are three forms of unconventional natural gas currently in production in the U.S.: tight gas, shale gas, and coal bed methane. Each has various issues associated with production, although there are also several key similarities.

1. **Tight gas** is produced mostly from low-porosity sandstones and carbonate reservoirs. Often the natural gas is formed thermogenically outside the reservoir, such as in adjoining coal-beds, and migrates there over the course of several million years. As the formations are often highly compact, hydraulic fracturing is almost always necessary to allow movement of gas to the surface. Wells drilled to extract tight gas are some of the deepest, extending up to 3,000 meters below the surface.
2. **Shale gas** is derived from tightly packed shale formations that also contain methane (and substantial amounts of kerogen, the key ingredient in oil shale). Layers in the rock formed as a result of sediment and organic matter deposition in deep water basins. After long periods of time, this bedding lithifies and allows for little horizontal movement, and almost no vertical movement. Because organic matter is deposited along with sediments, these formations are both the source and the reservoir of the natural gas.
3. **Coal bed methane** is one of the most prominent emerging sources of natural gas, and is found bound tightly in coal seams. Coal beds, like shale, are both the reservoir and the source of methane, as it becomes trapped when the organic matter that formed the coal decomposes. The distinguishing issue associated with CBM, often less prominent in other sources, is the tremendous volumes of groundwater stored in coal beds. Because reservoirs are typically shallower, potential issues with proximity to groundwater sometimes prevents extensive hydraulic fracturing. CBM produced water typically must also be pumped to the surface before methane can be released, which can create issues with disposal and usage in an arid west (DOE, 2009).

Drilling and Exploration Background and Impacts

During the process of exploration, wells are drilled to depths of around 5,000 feet and special petroleum detection instruments are lowered to determine if natural gas is present in high enough quantities for cost-effective extraction (Hock and Middleton, 2010). This process utilizes mainly fresh water for coolant and lubricant. Once the well is determined to be productive, it is lined again with concrete to prevent leaching into groundwater and to provide a contained modem for natural gas to escape when it is being pumped to the surface. The beginning of completion requires what is probably the most controversial and debated component of the drilling process: hydraulic fracturing.

This process involves injecting tremendous volumes of water, sand and other chemicals into a natural gas-containing formation at very high pressure, causing the rock to fracture and providing a pathway for it to move towards the wellhead and up to the surface. It is the chemical composition of this "fracking fluid" that is of primary concern to public health and wildlife officials; coupled with the fact that miniature earthquakes generated from each fracture are believed to be causing disturbances in groundwater flows and chemistry.

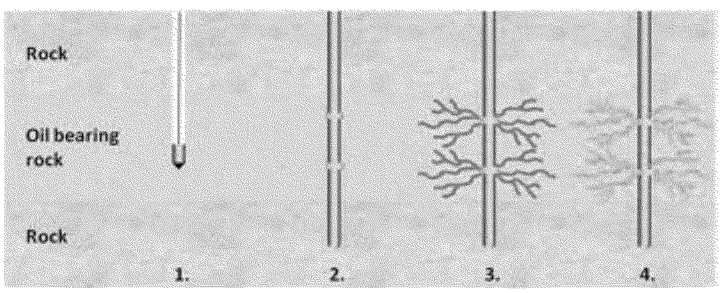

Figure one: Schematic of hydraulic fracturing process, from drilling to natural gas flow to the wellbore. www3.imperial.ac.uk

Fracking became part of natural gas extraction beginning the in 1960s, and became widespread during the natural gas boom of the early 1990s. Some conventional wells may still manage to be productive without it, but it is used in the vast majority of completions to enhance natural gas recovery. The goal of fracking is to create a highly conductive fracture system that will allow rapid flow of natural gas through the methane-bearing zone to the producing well. (EPA, 2004). Many natural-gas bearing formations are so tightly packed that without increasing their porosity there is little opportunity for movement of gas toward the wellbore for extraction. Hydraulic fracturing first injects fluids to initiate fractures, and then transports proppant (typically sand) into the formation to maintain uplift while the gas is allowed to flow towards the well.

The industry firmly states that their drilling and extraction processes have minimal impacts to surficial and groundwater systems. The depths to which they drill and extract natural gas are typically thousands of feet below normal residential wells, which they believe should not allow contamination by fracking fluid. They also utilize water treatment facilities, transportation pipelines, pond linings, and numerous other preventative measures to preserve water quality (EnCana, 2010; ExxonMobil, 2010). Despite all their efforts and claims, residents near drilling activities can sometimes have such high concentrations of methane in their tap water that holding a lighter to it can actually cause it to ignite (Fox, 2010). Contaminated waters full of hydrocarbons (like methane, CH_4) sometimes create a plume of contaminants in groundwater surrounding wells (Kharaka et al., 2007). Water protection coalitions are concerned and speaking out; therefore, one must ask where the truth falls in this debate: is drilling an environmentally safe activity, or are advocacy groups and residents correct in their accusations?

There is one other well-known form of water generated in the drilling and extraction processes. Produced water is the term given to water that also resides in natural gas-bearing formations and must be brought to the surface along with the natural gas. There are several factors of concern associated with this water. One is simply the sheer volume associated with some formations, and although the amounts and composition vary by location and type of natural gas, they have the potential to strain receiving water bodies and deposit contaminants. Produced waters are typically stored underground predominantly in permeable formations like aquifers and porous coal beds (Johnson et al., 2007).

It is estimated that on average in coal bed methane production (not tight-gas or shale gas) there is one to eight ft^3 of water for each cubic foot of natural gas. Some researchers believe produced waters represent the single largest waste stream from oil and gas exploration and production, and have become a major factor in the feasibility of natural gas development (Mondal and Wickramasinghe, 2008). These waters are often highly saline and have high concentrations of heavy metals.

Fracking fluid and produced water often mix before they are brought to the surface, generating a potentially dangerous concoction of synthetic chemicals, petroleum byproducts, and heavy metals. While the industry takes precautions to prevent this water from entering local waterways, pipelines burst, trucks spill, and holding ponds can leak or overflow. Thus, it will be crucial to examine the impacts of these accidents to surface water systems as many towns, particularly those in the west, depend on these water bodies for their municipal, agricultural, and industrial water. For purposes of this study, we will define the produced water, fracking fluid, and other water leftover from the process of drilling and completion activities collectively as "wastewater."

Industry Practices to Minimize Pollution

Many of the energy companies in the area have implemented what they believe to be adequate facilities and best practices to protect the environment and people. EnCana, the largest natural gas producer in the Piceance Basin, asserts that they put forth a concerted effort to minimize their environmental impacts. They employ a dissolved air flocculation water treatment plant for their produced water, 90% of which they recycle. The rest is reinjected into inactive wells and monitored so as to not exceed the volumetric limit of the underground well.

While their treatments do not completely remove hydrocarbons, iron, or total suspended solids, they do meet compliance levels of the Colorado Department of Public Health and Environment. EnCana's Environmental Group conducts water and air sampling, responds to spills, and is responsible for the reclamation of well pads (Hock and Middleton, 2010). They also have an Environmental Innovation Fund that "offers opportunities for us to partner with initiatives that enable more efficient water use for future generations" (EnCana, 2010).

Other major companies like Halliburton are also taking measures to reduce their environmental impact on some level. Their "CleanStream Service" utilizes ultraviolet light technology to control bacteria (that can interfere with drilling operations) instead of harmful biocides. Also like EnCana, they utilize facilities that treat and recycle residual water to be used in their drilling and completion operations (Halliburton.com).

Antero, another company with a major presence in the Piceance Basin, uses pitless drilling to prevent the problems typically associated with pits like leaking liners and volatile organic compounds (VOCs). They recycle 90-95% of their produced water and deposit the rest into three injection wells in Garfield County. They are currently moving towards a new treatment option that involves the use of biochemistry to remove up to 98% of sulfates, hydrocarbons, and VOCs instead of the traditional flocculation methods that have a much lower removal rate (Antero Energy, 2010).

Federal Loopholes in Water Protection for Natural Gas Producers

The controversy surrounding the use of hydraulic fracturing is steeped in political posturing. In 2005, Vice President Dick Cheney's Energy Policy Act exempted this process from the Safe Drinking Water Act (SDWA). The SWDA was passed by Congress in 1974 to protect public health by regulating contaminants in the nation's drinking water supply. It authorizes the EPA to set national standards for drinking water to protect against both naturally-occurring and man-made contaminants. (EPA, 2004).

Citizens would generally like to believe that this ensures water coming from municipal water supplies (and from domestic wells) will be clean and safe for them to drink. Thus, there has been a great deal of upset among environmental groups and citizens since an exemption, notoriously called the "Halliburton Loophole" by environmental groups, was passed that threatened this right. The *New York Times* accurately represented the feelings of many when they stated in 2009: "The safety of the nation's water supply should not have to rely on luck or the public relations talents of the oil and gas industry."

The Energy Policy Act, Section 322, Hydraulic Fracturing, states that Paragraph (1) of Section 1421(d) of the Safe Drinking Water Act (42 U.S.C 300h(d)) should be amended to read that the term underground injection means "the subsurface emplacement of fluids by well injection and excludes – (i) the underground injection of natural gas for purposes of storage and (ii) the underground injection of fluids or propping agents (other than diesel fuels) pursuant to hydraulic fracturing operations related to oil, gas, or geothermal production activities." This section has since prevented natural gas companies from being forced to reveal the constituents of their fracking fluid to regulatory agencies and the public for what they claim are proprietary reasons.

The natural gas industry is also exempt from several key provisions of the Clean Water Act, the fundamental law that protects our nation's waters. The act typically requires a permit for storm-water water runoff from industrial operations and facilities. However, since 1987, the oil and gas industry has not been required to have a permit as long as stormwater discharges from well pads and compressor stations are uncontaminated (Mall, 2007). Given current knowledge about contaminants present, there is little ability to ensure this is the case.

Many natural gas operations, like road construction and well pads, also remove vegetation from large swaths of land and allow large increases in sediment loading to nearby streams and rivers. Natural gas companies are not required to put erosion prevention measures in place despite the well-established fact that sediment can cause severe problems for aquatic life and municipal water treatment. Some definitions used in the CWA are problematic as well: chemicals used in fracking fluids are not designated as "pollutants," and many of the intermittent stream waters that they may contaminate are not considered "navigable," a status that would qualify them for greater protection.

Natural Gas Production in the Piceance Basin

While many areas of heavy drilling activity have seen substantial research and study on the effects of wastewater on their water quality, the Piceance Basin of Western Colorado has relatively little literature published on this subject. This region has seen high levels of natural gas activity and necessitates more information regarding the specific compounds present in wastewater there and how this may impact surface water. The Piceance ranges east to west from Glenwood Springs to Grand Junction, and north to south from Rangeley and Meeker to Delta. It includes Garfield, Rio Blanco, Pitkin, and Delta Counties. For this study, we will focus mainly on the southern portion of the basin and the towns incorporated into Garfield County.

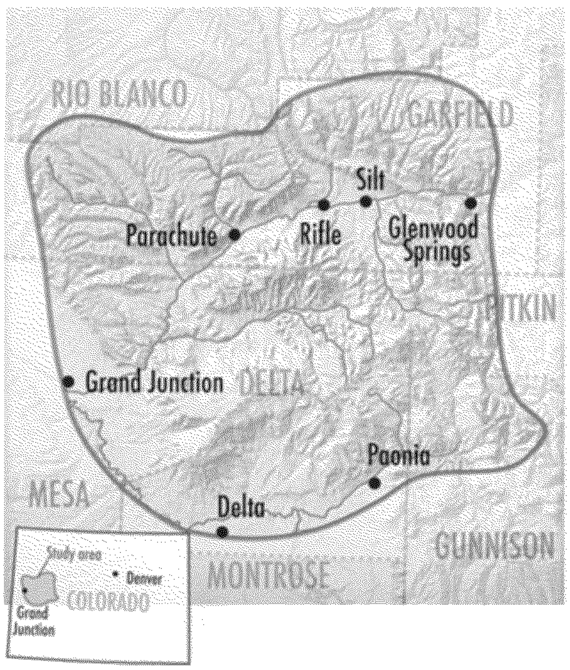

Figure two: the Southern region of the Piceance Basin, Colorado (US Geologic Survey)

Geology of the Piceance Basin

The geology of the Piceance consists primarily of three formations: the Wasatch Formation, the Mesaverde Group, and the Mancos Shale. The Wasatch Formation is the overlying strata of most of the region. Underlying it is the Mesaverde group, which is composed of two different formations: the Iles and the Williams Fork Formations. These are the most pertinent to our study because they are the primary producer of natural gas in the area is the Williams Fork. The Williams Fork Formation was named for its outcroppings along the Williams Fork River near its junction with the Yampa River along Moffat County, CO. It is thickest along the eastern portion near the Grand Hogback at approximately 474 m (at a depth of 1100 m – 1.571 m). It becomes narrower as it moves west, decreasing in thickness to about 370 m near the Colorado-Utah state line (Hettinger and Kirschbaum, 2002).

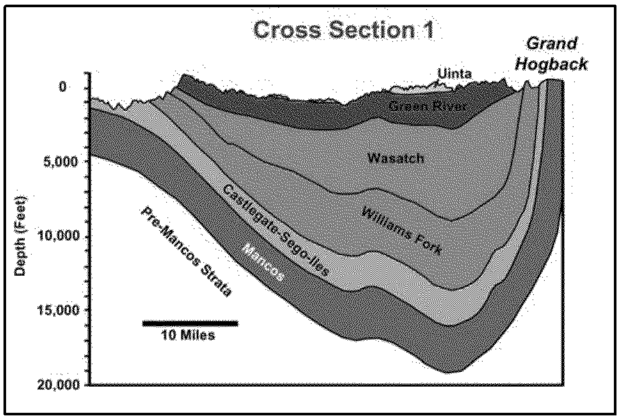

Figure three: The geologic strata of the Piceance Basin, from Grand Junction (left) to Glenwood Springs (right). Cole and Pranter, 2009)

The Piceance Basin consists mostly of interbedded non-marine shale, sandstone, and coal. The Mancos Shale was deposited in costal-plain and braid-plane environments that include ponds, lakes and marshes (Yurewicz et al, 2006). The gas that accumulated in the basin was generated from abundant gas-prone source rocks that were in close proximity to low-permeability sandstone reservoirs. As the gas generated from the coal formations began to increase, it began to migrate into adjacent sandstones. Because these sandstones had such low permeability, the rate of entry into the formation exceeded that of its loss, and a gas reservoir was formed (Cumella and Ostby, 2003). Garfield County contains all three types of natural gas (coal bed methane, shale gas, and tight-gas) in these formations, but tight gas from low-permeability sandstone is currently seeing the highest rates of production.

Constituents in Fracking Fluid

Many of the sources for water contamination come from fracking fluid. Under pressure from the EPA and the Colorado Department of Public Health and the Environment (CDPHE), some companies have recently reported what may be included in their fluids. While concentrations and usage of certain chemicals can vary by company, the Garfield County website lists some of the key compounds (Garfield County Oil and Gas Department, 2009). It does provide a disclaimer that readers should understand toxicological effects are associated only with certain concentrations and exposure pathways. Even household cleaning agents may be lethal in high concentrations, just fracking fluid constituents may be harmful only in certain concentrations.

The constituents listed on this website can be helpful in gaining knowledge about what is used in fracking fluid, however, the list is not comprehensive. Hundreds of compounds can be used in a given fracking operation. It also claims that these compounds are lethal or toxic only in high concentrations, however, this statement has little benefit to researchers or residents considering there is currently no legislation forcing companies to release the concentrations they use. Regardless of the individual companies' intellectual property rights, without such regulation, it is possible that some compounds could be present in high enough concentrations to be problematic.

Chemicals used in fracking can generally be grouped into fourteen types. There are a number of lists regarding these classifications, all of which cover similar subjects. Each are key in understanding why the industry insists on adding chemicals to their drilling and fracking processes. This list was obtained from a paper written by Theo Colburn, founder of the Endocrine Disruption Exchange (TEDX) in 2010.

Fracking Fluid Constituents

Acids	To achieve greater injection ability or penetration and later to dissolve minerals and clays to reduce clogging, allowing gas to flow to the surface.
Biocides	To prevent bacteria that can produce acids, eroding pipes and fittings and breaking down gellants. This ensures that fluid viscosity and proppant transport are maintained.
Breakers	Allows the breakdown of gellants used to carry the propant, added near the end of the fracking sequence to enhance flowback.
Clay stabilizers	To create a fluid barrier to prevent mobilization of clays that can plug fractures.
Corrosion Inhibitors	Reduces the potential for rusting in pipes and casings.
Crosslinkers	To thicken fluids often with metallic salts in order to increase viscosity and proppant transport.
Defoamers	To reduce foaming after it is no longer needed in order to lower surface tension and allow trapped gas to escape.
Foamers	Increases carrying-capacity while transporting proppants and decreases the overall volume of fluid needed.
Friction reducers	To make water slick and minimize the friction created under high pressure and to increase the rate and efficiency of moving the fracking fluid.
Gellants	To increase viscosity and suspend sand during proppant transport.
pH control	Maintains the pH at various stages using buffers to ensure maximum effectiveness of various additives.
Proppants	To hold fissures open, allowing gas to flow out of the cracked formation. It is usually composed of sand and occasionally glass beads.
Scale control	To prevent build up of mineral scale that can block fluid and gas passage through pipes.
Surfactants	To decrease liquid surface tension and improve fluid passage through pipes in either direction

Many of the constituents in fracking fluid are manufactured by supply companies like Halliburton (who also has their own drilling operations) and Weatherford, and then sold to drilling companies like EnCana and Williams. A list of common constituents in fracking fluid may consist of chemicals like gluteraldehyde, 2-BE (Ethylene glycol monobutyl ether), and Chloroxylenol, used as biocides in drilling mud; Polyacrylamide, used in the flocculation of solids; and Poloxamer 181 (Polyethylene-polypropylene glycol), which increases the solubility of oily substances. While some substances like hydrochloric acid are used to prevent scale buildup, most constituents are organic compounds.

Compounds in Produced Water

Produced water, particularly from coal bed methane, has been researched extensively in many regions affected by natural gas. It is known to contain concentrations of heavy metals, be highly saline, and, in many cases of natural gas production, contain high levels of organic compounds. Many of these can be toxic to humans, including the family of compounds benzene, ethylene, toluene, and xylene (BTEX). This group is commonly found in diesel fuel, which was formerly a typical constituent in fracking fluid. However, it has recently been phased out by many companies because of these toxic properties (Halliburton, 2010). However, many waters that co-reside in natural gas containing formations have high concentrations of this compound because of their close contact with petroleum products, and they have recently turned up in numerous studies on the impacts of natural gas activity to water quality.

Coal bed methane has been more heavily studied than other unconventional sources, largely because the volumes of water generated are much greater and can be used more extensively for human purposes. However, many characteristic compounds of coal bed methane produced waters have been detected in most types of produced water. Therefore, we can compare the characteristics of coal bed methane produced waters to those of tight gas like that being extracted in the Piceance Basin. This comparison provides a helpful level of background information on the subject.

The Powder River Basin- an example in Coal Bed Methane Produced Waters

The Powder River Basin of Wyoming and Montana has sparked the interest of numerous researchers who have generated significant literature on produced water. This is largely because many consider that region to be the fastest-growing coal bed methane development area in the United States (Ganjegunte et. al., 2008). In the Powder River Basin, natural gas produced waters are used extensively for agriculture irrigation and livestock ranching, increasing its distribution and exposure to plants and animals. This necessitates an understanding of these impacts as well as provides an excellent case study for its potential impacts to soils.

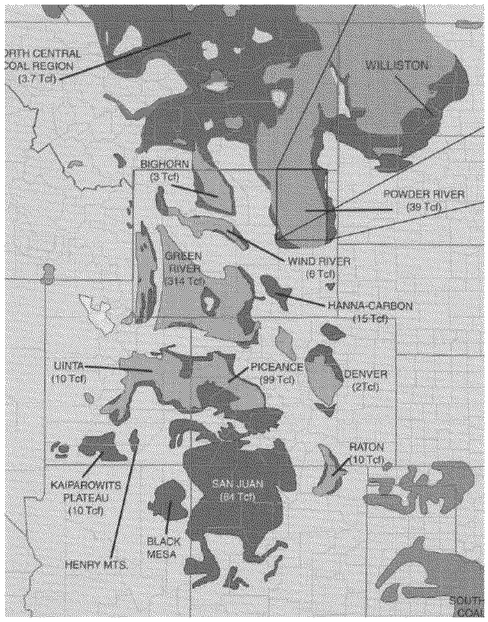

Figure four: The major natural gas-producing regions of the Intermountain West (Bryner, 2002)

The Powder River Basin is dominated by smectite clays, which are often characterized by poor drainage and have a high potential to be damaged by the organic and inorganic compounds associated with CBM produced water. In a study where produced waters were applied for one to four years, it was found that they are high in sodium (Na^+) and bicarbonate (HCO_3^-) and that they have the potential to lead to soils that have salinity several times that of seawater. While a high chloride concentration affects the ability of plants to uptake water, elevated sodicity in irrigation water impedes plant growth due to poor physical conditions. Of all the cations, Na^+ has been found to have the greatest impact on receiving systems. It adversely affects the soil structure necessary for water infiltration, nutrient supply, and plant aeration by causing aggregate breakdown (Johnston, et. al. 2008; Brinck and Frost, 2009).

The measure of sodicity is typically described by the sodium adsorption ratio (SAR). This is a measure of the concentration of sodium relative to magnesium and calcium, because the two tend to have opposite effects on soil properties. The SAR is defined as:

SAR (mmol/L) = $[Na^{+}] / [Ca^{2+} + Mg^{2+}]^{1/2}$

Sodium causes clay particle dispersion and aggregate breakdown largely due to its large size and single positive charge. Because it is monovalent, it fully fills the valence electrons of clay particles and thus reduces their ability to bond to each other. If clays become saturated with sodium ions, dispersal may occur depending on the ionic strength of the solution. Calcium and magnesium, on the other hand, bond to clay particles and leave one electron remaining for another clay particle to fill; this increases soil stability and flocculation.

There are several other ecosystem impacts of increased salinity and sodicity discovered from studies in the Powder River Basin. High chloride concentrations could pose obvious problems for organisms that would have difficulty adjusting to waters of this ionic strength (up to 384,000mg/L). Elevated salinity also affects the ability of plants to uptake water, which they need to facilitate biochemical processes such as photosynthesis and plant growth. It dehydrates soils much as salt absorbs water when we throw it on our sidewalks to melt snow and ice.

Coal bed methane produced water is typically saline, neutral to slightly alkaline, highly sodic, and anoxic to slightly oxic. The primary ions are sodium, carbonate, and bicarbonate. Common trace elements include aluminum, arsenic, barium, boron, copper, iron, manganese, nickel, selenium, and zinc (Rice, 2000; Johnson, et al, 2008). Release of CBM water into these watershed soils may increase pH and solubility and mobility of many of these elements, leading to further potentially damaging effects (McBeth et. al., 2003). Mercury is also emerging as a key environmental danger present in many produced waters, with some states actually issuing fish consumption advisories for dozens of lakes and streams because of the high bioaccumulation of mercury in sport fish (Ryan, 2009).

Many previous studies have indicated that coal bed methane discharge waters have high concentrations of organic compounds that are often present in concentrations that can be harmful to surrounding organisms. In wells and streams, compounds have been detected that include polycyclic aromatic hydrocarbons (PAHs) and their derivatives: biphenyls, phenols, aromatic amines, phthalates, and heterocyclic compounds containing nitrogen, oxygen, and sulfur. The sulfur-containing heterocyclic compounds included dibenzothiophene and benzothiazole, which are both significantly toxic to aquatic organisms and potentially to humans in drinking water (Ryan, 2009). In regards to the effects of these contaminants on aquatic life, Stromgren et al (1994) found that the toxic effects of produced water on organisms may be due to adsorption of water-soluble components through their surface epithelia, and/or ingestion of particulate material.

Many of these compounds are known to be carcinogenic depending on the concentrations present in water. PAHs and their derivatives were identified most frequently in samples collected in some studies, likely because of leaching from sub-bituminous coal. Acute exposure to high concentrations (0.2 μg/L) of specific PAHs can cause red blood cell damage, anemia, suppressed immune-function, and hormonal defects like development and reproduction (Orem et. al., 2007). Volatile organic compounds (VOCs) like benzene are also fairly common in produced water. Many of these PAH compounds of higher molecular weight (4-6 rings) are known carcinogens, causing damage through enzymatic conversion of epoxides in the body and subsequent adduct formation with cellular deoxyribonucleic acid (DNA). While the health and environmental impacts of long term exposure to these compounds is unknown, researchers were relieved to find that the PAHs observed in produced water from the Powder River Basin had mostly lower molecular weight and thus were generally much less harmful to human health.

It is important to ensure that elevated salinity does not cause negative impacts to soil and water quality because many produced waters are land-applied for agriculture and ranching in the Powder River. It is possible to actively treat produced water through the use of reverse osmosis and nanofiltration, which allow for less damage to soil and receiving water bodies. However, most natural gas producing companies do not prefer these methods because of their high costs. Soil amendments such as gypsum (CaSO4) are frequently utilized because they are relatively inexpensive and effective. Gypsum reduces clay-particle dispersion by: (1) increasing the electrical conductivity of the soil solution the diffuse double layer of ions surrounding the clay particle, and (2) it displaces Na^{+} with Ca^{2+} on the exchange sites. The sodium is then mobilized and can leach below the rooting zone with excess irrigation water (Brinck and Frost, 2009).

Compounds in Oil Shale Produced Waters

Wastewaters generated from oil shale drilling and production can be very similar to coal bed methane, and present similar problems in disposal and treatment. Up to 22 gallons of contaminated water can be generated for every gallon of shale oil, and many believe this will also influence the economic viability of oil shale on a large scale. Oil shale wastewaters typically have high concentrations of dissolved organic compounds, some of which are strong complexing agents. Complexing ability refers to the strength of the ligand to bond metals and other organic compounds. Because many of the compounds in oil shale retort waters resist degradation by conventional activated sludge wastewater treatment, they remain present in water for long periods of time. Pyridine, quinoline, and their alkyl derivatives, all found in the hydrophobic base fraction of the wastewaters, are known to form highly stabile complexes with a variety of metals (Stanley and Sievers, 1985).

Several of the prominent studies regarding oil shale waters have also examined volatile organic compounds, which generate much of the concern related to health impacts. Hawthorne and Sievers conducted a study in 1984 that examined the emissions of organic air pollutants from shale oil wastewaters, comparing them to those found in a typical urban air sample contaminated with pollution from car exhaust and coal-fired power plants. Using a headspace analysis and purge and trap analysis, they found both benzene and pyridine and their alkylated derivatives. Because exposure to air often initiates many of the reactions involved with this process, wastewaters exposed to air emitted approximately three orders of magnitude greater quantities of organic compounds than an equal amount of wastewater held in a closed container with an equal air headspace.

Fate and Transport of Natural Gas Wastewaters

There are many unanswered questions about the fate and transport of wastewaters from natural gas activities. Many sources, like the EPA and the industry, state that the majority of drilling and fracking fluids injected are removed during extraction leaving a low chance of migration away from the intended formation. However, some studies have shown that over 50% of fluids can remain within a well after it is completed (Sumi, 2005). In British Columbia, an area also experiencing an expansion of the shale gas industry, "fracture communication incidences" have caused fracking fluids injected into one well to emerge in other wells up to 670 meters away. There is little way to know exactly how these fluids will move: "As soon as highly pressurized fracking fluids gets through the cracks that you have created and reaches a joint system that has been there for many years, the joints open in unpredictable ways" (Nikiforuk, 2010).

Organic compounds, which make up the bulk of our study analysis, can play a significant role in the binding of heavy metals from produced water. The fate of metals from wastewaters in streams and hyporheic zones is primarily influenced by metal speciation. Most metals are removed by adsorption to settling particles, minerals, and organic matter in the hyporheic zone. However, changes in concentration or introduction of these organic compounds such as benzothiazole can have an effect on the way metals precipitate and co-precipitate on streambeds. Metal speciation is also believed to be affected by photoreduction of ferric oxyhydroxide colloids, which results in variations in the metal concentrations present in streams (Ryan, 2009). Both chemical binding and physical transport are essential in understanding the level to which contaminants can impact water supplies and thus human health.

Thermogenic vs. Biogenic Methane

Several previous studies conducted in the Piceance Basin have indicated that natural gas activities are increasing the migration of methane and other petroleum products towards earth's surface. One way to identify if this is occurring is through testing for the presence of different types of methane (CH_4) based on their carbon signature. Thermogenic methane is created as a result of temperature and pressure far below the earth's surface, and typically resides in the coal beds where it was formed (Scott, 1994). Predominantly found in the Williams Fork Formation, this is typically the commercially produced type. Isotopic analysis reveals that the ratio of C^{13}/C^{12} is lower in thermogenic methane because it has been given ample time to degrade. Biogenic methane, also commonly called "swamp gas," is created through microbial respiration. It is what we typically find being released from wetland and pond bottoms, hovering over landfills, and from decomposing food within animal bodies.

Measuring the ratio of thermogenic to biogenic methane can be an extremely effective way to measure the movement of natural gas and the fluids associated with it. While many streams (especially those with wetlands nearby) will have some concentration of methane present, these numbers have the potential to increase if natural gas activity causes seepage to occur through cracks generated by hydraulic fracturing. If methane concentrations are determined to be predominantly thermogenic in origin, it may provide evidence that migration out of the target formation is occurring. Below are some examples of when it was believed this was the case, and how it may point to future areas of concern.

2004 West Divide Creek Natural Gas Seep

Perhaps one of the greatest fears related to fracking fluid is its almost completely unknown movement within drilled formations. Are industries proponents correct in saying that water remains in the intended formation or is get almost entirely removed during the extraction process? Or are pathways generated that allow for its movement into residential wells and surface water? Many residents and researchers in areas surrounding development have observed the latter.

One of the most widely publicized and researched of these was the EnCana gas seep that occurred in 2004 as a result of faulty cement casing around a recently drilled well. Several landowners along West Divide Creek had observed flammable bubbles emerging from the creek, as well as the presence of iron-reducing precipitates and swaths of dead vegetation. While EnCana worked to remediate the site with tools such as implementing remedial cement casing and installing an air-sparging treatment downstream of the seep, thermogenic methane concentrations remain elevated.

Concentrations of benzene have declined substantially since the seep, although are still present in elevated quantities. Dr. Geoff Thyne, a professor from the University of Wyoming who conducted the bulk of the study, estimated that it will be after 2012 before benzene concentrations are below the maximum allowable limits (Thyne, 2010). While this mistake by EnCana was believed to be a relatively isolated incident, residents remained concerned that this indicates fracking fluid and other contaminants have the potential to move substantial distances from the target formation.

Mamm Creek- A Hydrogeologic Examination of High Levels of Tight Gas Drilling

Studies have been conducted on other affected streams in the Southern Piceance Basin, to examine both the impacts to water quality and hydrogeology of the area. Mamm Creek, just west of Divide Creek, is a high-production area that provides an excellent case study in how natural gas drilling could alter ground and surface water flows. In 2008, a study was conducted in evaluation of data collected in 2006 by URS Corporation. The report from 2008, written by Geoff Thyne of the University of Wyoming and entitled "Review of Phase II Hydrogeologic Study: Prepared for Garfield County," identified that there were elevated levels of several constituents of natural gas wastewaters in their sample data. Contributors to these samples were the URS Corporation (from their 2006 study), S.S. Papadopulos and Associates, ENCANA documentation, and a Colorado School of Mines thesis by Tamee Albrecht entitled "Using sequential hydrochemical analyses to characterize water quality variability at Mamm Creek field area, Southeast Piceance Basin, Colorado."

The results of this report confirmed that there was a relationship between petroleum activity and impacts to water quality. While these impacts were not to the level that exceeded regulatory limits at the time of this paper, there were some potential concerns; mainly elevated concentrations of methane and chloride in groundwater wells (Pg. 2). Pre-drilling values (from seven years earlier) of methane indicated less than 1 ppm, except in sites where biogenic methane was present in pond and stream bottoms. Through isotopic dating, it was revealed that elevated methane levels in most samples were thermogenic in origin.

The implications of these results indicate that while many natural gas companies would like us to believe there is little to no movement of produced water or fracking fluids out of producing formations, petroleum substances have been detected at the surface. Near the Divide Creek Anticline, where the largest numbers of problem wells were present, it was believed that increased use of fracking may cause a higher incidence of well drilling and completion problems. This in turn could affect water resources in the area (Pg. 8). In such a similar topographic and geologic area to Divide Creek, it is likely that similar affects may be observed.

US Environmental Protection Agency – Fate and transport of fracking fluid

In response to the high level of uncertainty and concern regarding the use of hydraulic fracturing, the EPA conducted a study in 2004 that examined not only the types of contaminants that may be found in the fluid, but also their fate and transport away from the original well. Studies reviewed in the literature found that hydraulic fracturing injection fluids could travel several hundred feet beyond the point-of-injection. They also found that because fractures are often much thinner than the original report (0.1 inch vs. 2 inches), the calculated volume of fluid that can fit within a fracture is less. This indicates that some fracking fluid must migrate into intersecting smaller fractures and that not nearly as much of it is recovered in the extraction process as was originally thought.

During the recovery of natural gas, wastewaters are pumped out of the formation through the producing well to reduce pressure, allowing methane desorption and extraction. Based on a 1991 study, however, only 61 percent of it was recovered. The EPA found this could be attributed to several factors. The first is a "check valve effect" that could trap some of the fracturing fluid upgradient of a collapsed or narrowed feature, preventing the fluid from flowing back into the production well. The high injection pressure used during fracking operations also causes fluids to flow away from the well at a much higher hydraulic gradient than occurrs during fluid recovery, causing some of the fracturing fluids to travel beyond the capture zone of the producing well. While movement into an aquifer can allow for dilution of some contaminants, such as BTEX (benzene, toluene, ethylene and xylene), it also presents concern over whether or not hydraulic gradients can cause migration into shallow groundwater.

The study's ultimate conclusion was that there is little threat to underground drinking water supplies as a result of hydraulic fracturing, and that no further study is needed. These findings produced outrage among environmental groups and even criticism from within the organization. Shortly after the report was published, Weston Wilson of the EPA called the study "scientifically unsound" and recommended further research. When it announced its new study on the effects of hydraulic fracturing on water quality, the agency reported that while the 2004 study concluded there was no significant impact to human health, "that same study has been widely criticized as insufficient and tainted by a bias toward the industry's point of view" (Colson, 2010). The industry has also maintained that there have been no reported cases of water contamination; however, industry critics claim that no cases have been found because no one was looking very hard.

The Oil and Gas Accountability Project (OGAP) claimed that the findings of the study excluded many important facts about hydraulic fracturing. In their report "Our Drinking Water at Risk: What EPA and the Oil and Gas Industry Don't Want Us to Know about Hydraulic Fracturing," OGAP points out that the EPA report only included information from coal bed methane studies, which constitute less than half of the natural gas in production today (DOE, 2009). The EPA also states that minimal drilling occurs within the drinking water portions of coal beds, and that there is little migration into other formations. However, other studies have been conducted that indicate as much as 50% of fracking and other production waters can migrate into adjacent formations.

Human Impacts

Natural gas activity is detrimental to humans on several levels. Noise pollution disturbs the peace of neighborhoods and ranches, 150-foot-tall drilling rigs reduce the aesthetic quality of residential properties, and compounds released into waters and air are thought to be damaging to human health. Many constituents in fracking fluids are believed to be harmful to humans; however, the benzene, toluene, ethylbenzene, and xylene (BTEX) found in produced water are some of the most well known and commonly found.

These are toxic in several ways, primarily in the nervous, hematopoietic, and immune system. According to the Agency for Toxic Substances and Disease Registry report on BTEX, acute or repeated exposure to any of the BTEX chemicals can produce neurological impairment resulting form when parent chemicals act on components of neurological membranes. It is believed this toxicity involves reversible intercalation in lipid bilayers of nerve membranes, which can yield changes in membrane fluidity; as well as possible interactions with membrane proteins that can cause conformational changes that impair nerve impulses. Animal studies have indicated that chronic exposure to high concentrations of toluene, ethylbenzene and xylenes can cause damage to liver and kidney tissues in the process of forming reactive metabolites.

The benzene component of BTEX is known for its concerns of causing hematotoxicity and carcinogenicity. The greatest toxic effect, characteristic of long-term benzene exposure, is likely a decrease in bone marrow cellularity, which evidence suggests ultimately leads to aplastic anemia and development of leukemia. It has also been classified as a human carcinogen by the National Toxicology Program, the EPA, and the International Agency for Research on Cancer. Much like the effects of all the BTEX components, acute inhalation or oral exposure can cause damage to the nervous system, resulting in symptoms such as dizziness, vertigo, tremors, narcosis, and cardiac arrhythmias. Benzene exposure can also result in immunological changes in both animals and humans, which are likely related to a decrease in circulating leukocytes and reduced ability of lymphoid tissue to produce the mature lymphocytes that form antibodies.

The hundreds of chemicals used in fracking fluid can have varying impacts to human health. The TDEX report on fracking fluid stated that there were twelve possible health effect categories for constituents. Many are used in multiple phases of the drilling and extraction processes, and some in dozens of different products. The effects can be chronic or acute, depending on the type of chemical, the duration, and the intensity of exposure. The most widespread health effect of these chemicals (more than 75 percent) was to the skin, eyes, and other sensory organs as well as the gastrointestinal system and the liver. Over half show effects in the brain and nervous system. These short-term effects would likely express themselves in the form of eye and skin irritation, nausea and/or vomiting, asthma, coughing, sore throat, flu-like symptoms, dizziness, headaches, weakness, numbness in extremities, and convulsions (Colburn, 2010).

Long-term health effects are also a large concern with many fracking chemicals. These are usually a result of more chronic exposure, and can often have even greater detrimental impacts. These included impacts to the nervous and immune system, kidneys, and the cardiovascular and blood. Over 25% of the constituents can cause cancer and mutations. A category designated “other” by Colburn also includes effects on weight, teeth and bones, and the ability to cause death. Finally, more than 40% of the chemicals used have potential ecological effects, including harm to aquatic and other wildlife.

Despite the industry’s constant reassurance that there are minimal impacts to air and water quality as a result of their presence, many residents of Garfield County believe they have experienced numerous and highly detrimental health effects as a result. Whether various regulatory entities have something at stake, or because these residents lack strong enough proof of causation, none of the reports or concerns have been legitimately acknowledged or validated. Many citizens feel that the media is their only means of raising awareness for their cause. For some, this exposure has caught the attention of legislators, commissioners, and other decision-makers. For others, it has been a long and hard fight to gain recognition of their issues and achieve action by those in power.

In her book *Collateral Damage*, author Tara Meixsell describes the ill health effects to residents she observed as a result of natural gas activity in Garfield County. After she and her husband moved to the area in 2001, she was amazed at the extent to which natural gas had overtaken the landscape. While not as personally impacted by the development, she found that many of her neighbors and friends had experienced damage to their property, pets, and health. Many of the cases seemed to be similar, with symptoms like headaches, dizziness, and nosebleeds. Sometimes, they claimed, the fumes from well pads were so intense it would cause them to lose their balance or collapse. Regulation has become stricter since many of the cases in the book, but incidents like this still occur.

The book primarily documents the story of Chris (Elizabeth) Mobaldi, who incurred several pituitary tumors believed to be due to carcinogens like BTEX in her water well. One of these required an intensive surgery that involved cutting open part of her skull to remove. She exhibited a number of symptoms of chemical toxicity and developed a strange and rare disease called "acquired foreign accent syndrome." Sometimes she would become unintelligible; attempting to speak but mumbling so badly that even her husband couldn't understand her. Meixsell also accounts of how the accent would change from time to time: one day Chris would talk like an Eastern European, and the next would have a choppy Asian sound. The Mobaldis did manage to get an accomplished lawyer on their case, but many are not so fortunate and merely receive a relatively small settlement in court.

Other residents in the area who feel their lives have been negatively impacted by the industry have used blogging websites to raise awareness and concern for the issue of these impacts. One website, Journeyoftheforsaken.com, describes what creator Lisa Bracken believes are incidences in which her and her neighbors have been affected by natural gas drilling as well as her own observations of the impacts of fracking on the creek that runs through her property. She, like many other residents in the area, has become highly concerned with the toxicity of fumes and chemicals used in drilling and fracking processes. Bracken also lost her father to pancreatic cancer in 2006; a disease she believes could be related to the high level of natural gas development in close proximity to their home. While carcinogenicity has been associated with several key fracking ingredients, a direct link to pancreatic cancer has not yet been established.

Through Journeyoftheforsaken.com, she cites cases in which she believes the industry has been highly irresponsible, putting profits before all else. Much like Tara Miexsell, she has gone to neighbors' houses to discuss matters related to the issue and seen near their homes unlined pits, leaking pipelines, and general destruction. They both believe regulators have been sluggish and irresponsive in their approach to these incidents, failing to take action in issuing fines or even investigating reports by residents.

In places like Pavillion, Wyoming, natural gas development has done so much damage to water quality that residents are actually being discouraged from drinking their water. In response to complaints from Pavillion residents in 2009 of strong odors and strange tastes associated with drilling, the EPA took samples from domestic and monitoring wells. Shallow groundwater was heavily contaminated with petroleum hydrocarbons and BTEX; it was found that the quality of drinking water in several domestic wells was unacceptable and may cause negative health effects.

While the EPA claims that it has not yet made any conclusions about source of this contamination, natural gas development seems to be the most likely culprit. As is often the case in this type of incidents, the company has agreed to help provide an alternate source of drinking water but admits no responsibility. The EPA is working with EnCana, the primary producer in Pavillion, to ensure that affected residents receive water and to address potential causes of contamination (Mylott and Abrams, 2010).

Much like Western Colorado, Eastern states that sit atop the Marcellus Shale formation are seeing explosive and often destructive expansion of the industry. This vast shale gas reservoir runs along the Appalachian Mountains from West Virginia to the western part of New York State. As a result, residents there also believe they have seen dramatic impacts to the water quality in their homes. Their stories add to the growing body of evidence that drilling and fracking may have more deleterious effects than many would have previously realized. In the town of Dimock, NY, the industry is transforming rolling hills and farmland into a network of roads and well pads. Families like the Saunters own properties that have lost much of their previous value as a result of this activity.

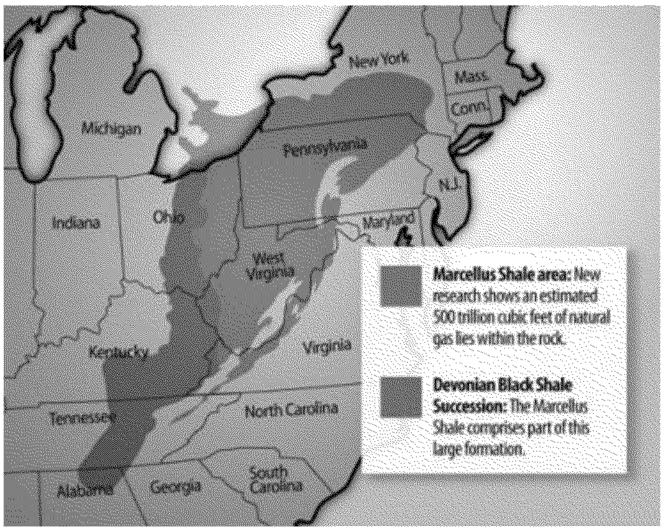

Figure five: the Marcellus (shown in red) and Devonian Black Shale (shown in blue) (Catskill MountainKeeper, 2010).

Only a month after drilling commenced on their property, the Saunters' water began to turn brown and highly corrosive, ruining their dishes and clothes. Cabot, the natural gas company believed to be responsible for the contamination, installed a water filtration system in an attempt to restore the Saunters' water quality. However, further testing revealed that the

Saunters' well was still contaminated, which they believed caused continued problems such as sores all over their son's legs and their daughter's dizziness after showering. Theirs is only one story among many. Problems have occurred on numerous properties in Dimock, with widespread cases of water contamination, a woman's water well spontaneously combusting, and domestic animals losing their hair in clumps (Bateman, 2010).

Impacts to land, water, and public health as a result of natural gas activity have been occurring for several decades all over the west in places like Colorado and Wyoming with relatively little national attention. Contamination has become a more prominent issue now that it is occurring in regions with more dense populations where entire towns may be affected. The vast reserves of the Marcellus shale formation assure that development will likely occur for years to come, but those whose lives are affected by the industry hope that better practices will be implemented. With numerous incidences of contamination from natural gas activity in that region, those affected all over the country are hopeful that greater attention will be paid to the issue and stronger regulations will be put in place.

Research Questions and Objectives

This research sought to indentify if natural gas extraction has an impact on surface and groundwater quality in the Piceance Basin. Since many compounds and chemicals from extraction are stated to be released only in small quantities, we attempted to analyze if they are found in levels that are appropriate for human and aquatic health. Knowing what may be present (both from produced water and fracking fluid), we identified compounds that are already believed to be in the water, as well as sought to determine if other compounds are present that were previously not well known but still pose a significant threat.

Hypothesis

Natural gas extraction is firm and somewhat harsh reality for the Piceance Basin. It provides a relatively healthy economy for nearby towns, and supplies Americans with a cleaner and more efficient energy source than coal or nuclear power. However, there are impacts to the environment and human health that may negate from these benefits. We hypothesize that while natural gas is a viable energy source that should be explored and utilized, natural gas extraction processes do generate wastewater that is present in concentrations that may be harmful to both surface and groundwater quality. We determined what level this is in our study in order to help all parties involved develop an understanding of how this energy source effects the environment around it.

As we have also discovered, it remains unconfirmed as to the movement of fracking fluid once it has been injected below the earth's surface. Little is also known about the movement of toxic groundwater and other hydrocarbons once fracking has occurred. Based on evidence from other studies investigating thermogenic and biogenic methane, we also hypothesize that there is migration of these contaminants that could allow them to enter surface and groundwater.

Significance and Broader Impacts

This research would yield results that may have widespread implications in the scientific community, policy decision-making, and the public eye. It would be substantially beneficial for a document to be published in the scientific literature that sheds light on how produced water and other forms of wastewater from tight sandstone gas wells can impact water quality, instead of focusing only on coal bed methane produced waters. The scope of this project is also meant to test for a variety of contaminants through the sample analysis methods to be used, focusing on those that are primarily of concern to public health. This could provide a pathway for other researchers to know the kinds of compounds to test for when analyzing these wastewaters.

Set to be completed this year, the Colorado School of Public Health (CSPH) also conducted the first ever Health Impact Assessment (HIA) of natural gas development in Battlement Mesa, Colorado. The Canadian energy company Antero has plans to drill several hundred wells inside the planned urban development this year, which has naturally caused concern among citizens, many whom are elderly and believe they are at increased risk of negative health impacts.

This HIA was requested by residents of the town "to provide the BOCC (Board of County Commissioners) with specific health information and recommendations relevant to Antero Resources Corporation (Antero) plans for natural gas development and production… CSPH worked in collaboration with Garfield County Public Health to conduct a qualitative and quantitative analysis of existing environmental, exposure, health and safety data pertinent to the Battlement Mesa community" (Witter, 2010).

As part of an Outreach Project through the University of Colorado at Boulder, we were able to contribute to the CSPH's data on water quality in Battlement Mesa by taking samples of both the intake and the output of the water treatment plant there which supplies essentially all the water to residents within the community. While sampling would ideally continue throughout the duration of natural gas activities, our samples were able to provide a snapshot of the quality of water entering and leaving the plant.

Finally, the attitudes and opinions of the public could stand to be swayed by the news that their water supplies and fishing locations are affected by an industry that surrounds them daily. Many water advocacy groups and local citizens are concerned with this issue, one that has spurned the action of the EPA, the US Geologic survey, the Bureau of Land Management, and multiple other consulting firms and municipalities. Conclusions made in our study will be able to further aid these organizations in their research and programs, as well as inform those affected by drilling how they may begin to take action in mitigating these impacts.

Research Description: Approach and Methods

This study was conducted primarily in three phases: (1) literature research and compiling previously collected data, (2) interviews with individuals involved in and affected by natural gas extraction and (3) quantitative primary data collection involving field sampling and laboratory analysis. Background research, sampling, and writing of the final report was conducted primarily by undergraduate Morgan Hill, who has background knowledge based on her education and work with professors. Prof. Joe Ryan is a professor in the department of Civil, Environmental, and Architectural Engineering at the University of Colorado at Boulder with years of experience and research working with water quality analysis. Sample analysis was conducted mainly by Profs. Mike Thurman and Imma Ferrer, who both have high levels of expertise in the LC/MS technology utilized in this study.

Literature review

While information and data is available regarding water quality in the Piceance, it is largely in a scattered array of various kinds of reports and from disparate agencies that have not cooperated in their research. Many energy companies have data from their environmental monitoring groups, but it is typically arranged in a format that is inaccessible to non-experts (which includes most town officials and concerned citizens). Therefore, it was a necessary part of the research process to compile data from other sources not published in the scientific literature to understand exactly how we could best add to the body of knowledge on this subject.

Much of the information on natural gas activities' environmental impacts generated from the Piceance Basin is in the form of government reports published by the state or Garfield County. Typically, a consulting firm or university collaborated on the research efforts. It was valuable to look at case studies of other streams and locations that yielded results indicative of migration of wastewaters from natural gas to shallow groundwater wells and surface wells.

Interviews with Experts and Local Government

To gain a better understanding of how natural gas can impact water quality and the work that is being done regarding this subject, we met with and interviewed numerous local experts, government officials, and municipal and county managers. This added to our collection of current data and research, as well as providing another facet of this research that was crucial to the outreach process: partnerships. Since, as we have previously mentioned, much of this research includes a cooperative effort between all parties working in the region, working with and knowing about all the players involved was highly beneficial.

We met with entities such as the US Geologic survey, Garfield County, Grand River Consulting (based out of Glenwood Springs), and industry representatives from major energy companies in the area. While there are smaller companies in the region, they are held to more lax environmental standards and therefore have less incentive to be environmentally conscious. EnCana is the largest producer in the area, and has also placed itself in a highly prominent position. The company currently has its own ecological research site and is the primary company representative for the Piceance Basin Water-Quality Data Repository. Other companies involved in natural gas extraction there whom we did not meet with are Chevron, Genesis Energy, Petroleum Development Corporation, Shell Oil Company, Williams Production, and Marathon Oil.

This research also included an Outreach Project in which we identified the needs of citizens in Western Colorado and worked with them to solve problems related to their concerns from natural gas development. In this study, we spoke with town and county officials to identify what needs there are in understanding water quality issues. They had the opportunity to request our assistance, and the Outreach Foundation at CU chose to provide a grant in the order of $16,000 over the course of two years. This augmented source of funding allowed us to increasingly integrate our study with the community of Garfield County, presenting our findings to classrooms in the school district and working with local municipalities. If partnerships facilitated by this grant are achieved, it will allow us greater access for taking samples directly from treatment plants and at many crucial points along tributaries that may lie on private property.

Primary Data Collection

<u>Site Identification- Disturbed Locations</u>

Primary data collection for this project was the key phase in which we began conducting our own analysis of water quality. Multiple counties affected by intensive natural gas development in the Piceance, Garfield County is currently under the heaviest (20 years ago natural gas extraction was primarily in Rio Blanco County), and has the highest population. Since our analysis is largely concerned with public health, it was crucial to select a tributary/river that supplies substantial water to municipalities and agriculture and could potentially affect human health if compounds in harmful concentrations are found. Site selection involved identifying one to a few streams that can be classified as disturbed, clearly lying along areas of major natural gas development. There are several of these located in Garfield County.

For a known impacted stream, we selected West Divide Creek, the site of the largest methane seep in Colorado history. This was based off the recommendation of the Garfield County Oil and Gas Department, because the creek had seen heavy development recently and had not been as thoroughly studied as others in the area. It is also slated to see another 284 wells near the creek over the next few years (Colson, 2010), so a "baseline" water quality assessment could prove to be beneficial to residents and later researchers.

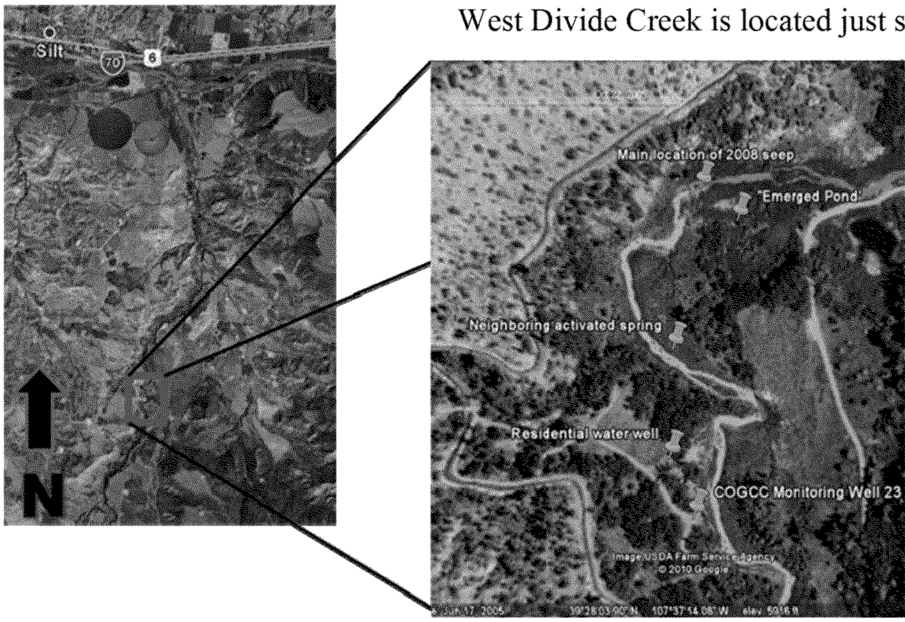

Figure six: main sample locations along West Divide Creek

West Divide Creek is located just south of Silt, Colorado. It is one basin east of Mamm Creek, the site of the 2006 study previously mentioned. It is a semi-arid environment. Vegetation classification is mostly piñon and juniper trees, which is also accompanied by cottonwood and scrub oak in areas of greater moisture such as those found near the creek. The highest point nearby is approximately 6,218 ft above sea level, while the lowest point, found in the streambed, is 5,470 ft. Water quality may also be affected by agriculture and ranching practices here, which deposit fertilizers, pesticides, and livestock waste into local water bodies. Many residents of the area own horses and cattle or grow crops like hay. Groundwater is also present in productive quantities, which provides drinking water for most residents of the area.

Due to limited time and funding, we collected 10 samples with two replicates each for a total of 20. The bulk of our affected samples were taken on the property of a resident along the creek who had observed impacts to the stream in 2008 when it was believed another seep had occurred. The sites selected on her property were locations where she had observed changes in stream color and clarity such as the formation of iron precipitates, foaming (much like that of surfactants, which is a common ingredient in fracking fluid), and vigorous bubbling from the streambed. One set of samples was taken from her drinking water well, in a location near the streambed that allowed for high levels of mixing between the two. 12 samples total came from her property.

Site Identification- Reference Locations

In an attempt to establish at least some level of background, samples were collected at a site that had been used as a reference location after the 2004 seep had occurred. Some level of natural gas activity has been underway above this location since then, but the bulk of natural gas development is occurring on the lower reaches of the stream. This was site was also on West Divide Creek, approx. two miles upstream of the known affected segment. Two samples with two duplicates were collected, one round from just north of a bridge that crossed the river at this location, and the other just south.

Main location of 2008 seep	39°28'07.55" N
	107°37'12.43" W
Emerged Pond	39°28'06.49" N
	107°37'11.58" W
Neighboring activated spring	39°28'03.81" N
	107°37'14.87" W
Residential water well	39°28'01.24" N
	107°37'15.99" W
ENCANA Monitoring Well 23	39°27'59.70" N
	107°37'15.74
2004 Seep Reference Location	39°26'37.17" N
	107°37'11.27" W
Battlement Mesa Water Treatment plant	39°26'18.38" N
	108°3'3.42" W

Table one: GPS locations of all sample sites

Also, to aid the town of Battlement Mesa in the water quality analysis portion of their Health Impact Assessment, we collected two rounds of samples from the water treatment plant just outside of town. Natural gas activity had begun there in the summer of 2010 by the Canadian company Antero. Earlier ideas for this study had anticipated that these results could provide a baseline in water quality. However, since drilling had already begun at the time of sampling, samples were taken to possibly indicate that no impacts had yet occurred.

The water treatment plant intakes 100% of their water from the Colorado River. Samples were collected at a spigot from the intake, and again at the output that is eventually sent to residents of the town. The water treatment plant utilizes conventional filtration methods that consist of flocculation, sedimentation, mixed media filters and chlorine for disinfection. The plant is capable of treating 6.5 million gallons per day while meeting the requirements of the EPA, but has yet to utilize its full capacity; it was designed by ExxonMobil in the 80s to supply water for a large population of workers for an oil shale industry that never materialized.

Sample Collection- Procedures

Much of the data collected on water quality in the Piceance Basin has come from taking a large number of samples and analyzing them for standard, common compounds. While this type of information is beneficial in developing baseline water quality data, it can sometimes miss compounds that are emerging in the scientific world or are only present in low concentrations. Our emphasis in sample collection was not on taking a large number of samples, but rather looking very thoroughly for a wide range of possibly harmful compounds in a smaller number of samples. At the time of this report, only 10 total samples with duplicates have been taken. Since the initial round of samples is mostly preliminary, it is hoped more samples will be pursued at a broader range of locations in future study.

Samples were taken in September 2010, during a low-flow period to provide a characteristic snapshot of present contaminants. In the process of sample collection, we closely adhered to the protocols of the Center for Environmental Mass Spectrometry, which corresponded closely with those of the USGS. All samples were collected in baked, glass, 1-liter, amber bottles complete with Teflon™ lined caps to ensure sample integrity. Bottles were filled to the top, and then closed with a cap containing sample fluid to keep bottle head space to a minimum. Each bottle was rinsed in the field three times with sample and filled to the top on the fourth sampling. Disposable gloves were used when taking the sample to prevent any personal care products from contaminating sample bottles. No use of insect repellant or consumption of coffee occurred during the sampling period.

Any unusual conditions concerning each sample were noted in a field notebook, copies of which were given to the lab for reference. Samples were stored in coolers with blue ice packs during transport from sampling locations, and then refrigerated until samples were extracted for analysis. Samples were labeled clearly with a permanent black pen and covered with tape for name protection. Bottles were wrapped in bubble wrap and taped to prevent banging and breakage of the bottles. Duplicates were taken of all samples for future analysis. Specific conductance and pH were recorded for each sample. All details related to sample collection and preservation will be recorded in a laboratory logbook. The logbook contains all relevant information including time and date of sampling, retrieval method, initials of sampler, sample identification number, and any other items of importance to sample characteristics.

Sample Analysis

Basic water quality characteristics were measured at the time of collection (and subsequently in the event that equipment was not working properly or field conditions did not allow for accurate readings). These were taken using techniques and equipment available in the lab of faculty sponsor, Prof. Joe Ryan. To test for conductivity (K), a common characteristic of produced water, we used a standard conductivity meter (Orion 122). A pH reading was also taken for each sample at the time of collection (Orion 250A meter and 9107 combination electrode).

Since the exact constituents of fracking fluid remain largely ambiguous, we devised a sampling plan for identifying them derived from the list posted on the Garfield County Website, the Endocrine Disruption Exchange report, and a list given to us by Roxana Witter at the

Colorado School of Public Health. Other compounds to be tested for have been identified in produced water from previous sampling done in the area and literature published on coal bed methane produced waters. While characteristics and composition of these waters differ by location, we can still expect to find some of them in the produced waters of the Piceance Basin. Knowing the chemical composition of these compounds from web database ChemIDPlus (http://chem.sis.nlm.nih.gov/chemidplus), we were able to estimate where they should lie on a chromatography chart. Distinction between compounds from fracking fluid and those from produced water was based largely off of these sources.

Organic contaminants were analyzed in nine of the samples taken by a variety of techniques available in the Center of Environmental Mass Spectrometry in the Department of Civil, Environmental, and Architectural Engineering at the University of Colorado at Boulder. Mass spectrometry will allow determination of the identity and composition of these contaminants through liquid chromatography/mass spectrometry-time of flight and liquid chromatography/tandem mass spectrometry with ion trap. Drs. Michael Thurman and Imma Ferrer, who run the lab, operated the equipment and identified the compounds present. Analysis methods were obtained from the lab.

Sample Extraction. An off-line solid-phase extraction (SPE) was used for the pre-concentration of the water samples. Extraction experiments were performed using an automated sample preparation with extraction columns system (GX-271 ASPEC, Gilson, Middleton, WI, USA) fitted with a 25-mL syringe pump for dispensing the water samples through the SPE cartridges. Water samples were extracted with Oasis hydrophilic-lipophilic balance (HLB) cartridges (500 mg, 6mL) obtained from Waters (Milford, MA, USA). The cartridges were conditioned with 4 mL of methanol followed by 6 mL of high performance liquid chromatography (HPLC) grade water at a flow rate of 1 ml/min. The water samples (100mL) were loaded at a flow rate of 10 mL/min. Elution of the analytes from the cartridge was carried out with 5 mL of methanol. The solvent was evaporated to 0.5-mL with a stream of nitrogen at a temperature of 45 °C in a water bath using a Turbovap concentration workstation (Caliper Life Sciences, Mountain View, CA, USA). The samples were transferred to vials and analyzed by liquid chromatography/time-of-flight mass spectrometry (LC/TOF-MS).

Liquid chromatography/time-of-flight mass spectrometry (LC/TOF-MS) analyses. The separation of the water extracts was carried out using an HPLC system (consisting of vacuum degasser, autosampler and a binary pump) (Agilent Series 1200, Agilent Technologies, Santa Clara, CA, USA) equipped with a reversed phase C_8 analytical column of 150 mm x 4.6 mm and 5 □m particle size (Zorbax Eclipse XDB-C8). Column temperature was maintained at 25 °C. The injected sample volume was 50 □L. Mobile phases A and B were acetonitrile and water with 0.1% formic acid, respectively. The optimized chromatographic method held the initial mobile phase composition (10% A) constant for 5 min, followed by a linear gradient to 100% A after 30 min. The flow-rate used was 0.6 mL/min. A 10-min post-run time was used after each analysis. This HPLC system was connected to a time-of-flight mass spectrometer Agilent 6220 MSD TOF equipped with a dual electrospray interface operating in positive ion mode, using the following operation parameters: capillary voltage: 4000 V; nebulizer pressure: 45 psig; drying gas: 9 L/min; gas temperature: 300 °C; fragmentor voltage: 190V; skimmer voltage: 60V; octopole RF: 250 V. LC/MS accurate mass spectra were recorded across the range 50-1000 *m/z* at 4GHz.

The data recorded was processed with MassHunter software. Accurate mass measurements of each peak from the total ion chromatograms were obtained by means of an automated calibrant delivery system using a dual-nebulizer ESI source that introduces the flow from the outlet of the chromatograph together with a low flow of a calibrating solution (calibrant solution A, Agilent Technologies), which contains the internal reference masses (purine ($C_5H_4N_4$ at *m/z* 121.0509 and HP-921 [hexakis-(1H,1H,3H-tetrafluoro-pentoxy)phosphazene] ($C_{18}H_{18}O_6N_3P_3F_{24}$) at *m/z* 922.0098. The instrument worked providing a typical mass resolving power of 15000±500 (*m/z* 922).

Total Organic Carbon

To gain a more complete understanding of the potential sources of organic constituents in each of the samples, we also conducted an analysis of total organic carbon (TOC). If our values were uncharacteristically high we believed this could indicate either migration of naturally occurring organic contaminants from hydraulically fractured formations or the presence of fracking fluids themselves. Dissolved organic carbon can reach concentrations of as much as 1000 mg/L in oil field brines, and volatile organic carbon from natural gas may be found in 100s of milligrams per liter. These unusual ground water concentrations receive DOC from organic matter derived from petroleum products (Thurman, 1985). TOC/DOC (minimum detection level: 02.mg/L) were measured using a Shimadzu TOC-V_{CSH} analyzer in the Environmental Center for Mass Spectrometry.

Specific Ultraviolent Absorption

The specific ultraviolet absorbance (SUVA) provides a helpful comparison of the total organic carbon present to what is naturally occurring. It is defined as “the UV absorbance of a water sample at a given wavelength normalized for dissolved organic carbon (DOC) concentration” (Weishaar, 2003). DOC/TOC constitutes the majority of organic matter in water, but contaminated samples can have moderately high TOC values that are not a result of plant matter. Thus, we were able to determine whether or not the TOC values we found were natural for that sample or from outside (and likely human-caused) sources. Our analysis for UV absorbance was conducted using a Hach DR 5000 spectrophotometer, in which the sample was measured at 254 nm against organic free water. Results were automatically reported in absorbance per centimeter. We then calculated $SUVA_{254}$ by dividing this value by the TOC to determine the ratio for eight of the ten samples.

$SUVA_{254}$ tends to increase with a when the contribution of organic carbon is primarly from terrestrially derived dissolved organic matter (a comparable measurement to dissolved organic carbon) (Jaffe et al, 2008). The Jaffe et. al. study also indicated that differences in $SUVA_{254}$ between sample sites could be attributed to microbially vs. terrestrially derived organic matter. Variations in dissolved organic matter (DOM) can also be attributed to spatial and seasonal changes. For example, we would be likely to find much higher concentrations of DOM in the spring, when snowmelt runoff carries large amounts of decaying plant matter over the surface. In the summer, the river is fed mostly by groundwater that has much lower inputs of organic matter.

Results

Results of our study can generally be divided into two categories based on analytic methods: TOC, which also includes a measurement of ultraviolet absorbance, and LC/MS. Together they helped paint a clearer picture of our findings.

Total Organic Carbon

Sample Name	Total organic Carbon (mg/L)
BM WTP Intake	2.9
BM WTP Outflow	1.8
WDC 2008 Seep	5.3
Emerged Pond	4.5
Domestic Well	5.7
EnCana Monitoring Well 23	4.1
WDC Rd. 346 Bridge	6.5
West of Dom Well	5.4

Table Two: total organic carbon values for eight of the sample sites

Our analysis measured TOC, however, DOC is often the value referred to in the process of describing the concentrations of organic carbon in water. TOC and DOC (dissolved organic carbon) are very similar measurements, as TOC is simply the sum of DOC plus suspended organic carbon or particulate organic carbon. Many scientists recommend separate measurements for each because TOC can fluctuate more greatly with precipitation influxes; DOC is also more chemically reactive because it measures individual organic compounds in the dissolved state. It is also a "reliable measure of the many simple and complex organic molecules making up the dissolved organic load" (Thurman, 1985). For purposes of this discussion, however, we will describe TOC to indicate the same results as those of DOC.

Concentrations of TOC vary widely with the type of water. Seawater and groundwater typically have the lowest values, with an average of 0.5 and 0.7 mg/L. "Colored" water from swamps or rivers during peak runoff typically have the highest values, sometimes reaching 30 mg/L. Lakes and rivers during moderate flows, with substantial inputs from groundwater, typically have 2 to 10 mg/L DOC. Interstitial waters of soil often have similar levels to that of surface water from streams and rivers. Transport of organic matter between various soil horizons as well as adsorption and decay processes in the soil typically causes DOC values to decrease with depth below ground. This decrease can also be attributed to removal by chemical and biological processes in the soil.

This analysis revealed fairly average values for surface water. The sample taken from Battlement Mesa's water treatment plant intake (labeled BM WTP Intake) showed TOC concentrations very typical of the Colorado River at 2.9 mg/L; the one-unit decrease in TOC for its output was also standard and indicates safety for human consumption. This indicates that its flocculation and sedimentation treatments are working properly to remove organic materials. Samples like the West Divide Creek Rd. 346 bridge exhibited fairly (although not abnormally) high values of dissolved organic carbon. This could be attributed to algae present in the streambed, or local agricultural and ranching activities. The three values for surface water taken from West Divide Creek were 4.5, 5.3, and 5.4.

TOC results of the two shallow groundwater wells indicated several interesting characteristics about their geology and hydrology. The first, EnCana monitoring well #23, showed what would be unusually high values of TOC had it been purely groundwater. This sample had both a brackish color and a strange smell typical of hydrogen sulfide (H_2S), both of which could indicate that TOC values might be higher than usual because of anaerobic activity. However, its concentration of 4.1 mg/L shows what would be normal for surface water. This indicates that there are high levels of mixing between ground and surface water in this region, and that this well was receiving high input from the alluvial floodplain of West Divide Creek, which is located only about 40 feet away.

The resident's domestic well also had what would be unusually high TOC concentrations for groundwater; however, the resident stated that there were nearly equal levels of groundwater and surface water going into the well. It is approximately twelve feet deep, which is far too shallow to be considered true groundwater. In the spring, snowmelt runoff has caused the river to rise nearly to the well saturating it to the level of shallow groundwater; later, in the summer, it lies approximately 30 feet from West Divide Creek. Therefore, after re-checking the calibration curve used in the analysis, we can assume that waters extracted from both of these wells are most likely interstitial soil waters, rather than true groundwater wells typically drilled to a depth of at least 90 meters.

Specific Ultraviolet Absorbance at 254 nm ($SUVA_{254}$)

Our analysis showed relatively but not a bnormally low $SUVA_{254}$ values compared to creeks and rivers in other studies. Often, rivers like the Colorado will have values around 0.03 $Lmg^{-1}cm^{-1}$. The $SUVA_{254}$ we calculated for the Colorado River (labeled as BM Water Treatment Plant Intake) showed 0.022 $Lmg^{-1}cm^{-1}$, and values for samples taken along West Divide Creek were all 0.018 $Lmg^{-1}cm^{-1}$ (with the exception of the Emerged Pond sample, which was not actually taken from West Divide Creek). However, aside from an extremely low value for the BM water treatment plant outflow, EnCana monitoring well 23 had the lowest $SUVA_{254}$ by a significant amount. In fact, the only lower naturally occurring $SUVA_{254}$ found in a study by Weishaar et. al. in 2003 was for the Pacific Ocean at 0.006.

Sample Name	**$SUVA_{254}$ Lmg-1cm-1**
BM Water TreatmentIntake	0.022
BM Water TreatmentOutflow	0.007
WDC 346 Rd. Bridge	0.018
Domestic Well	0.022
EnCana Monitoring Well	0.013
Emerged Pond	0.016
WDC 2008 Seep	0.018
W of Domestic Well	0.018

Table 3: SUVA Values for eight of the samples

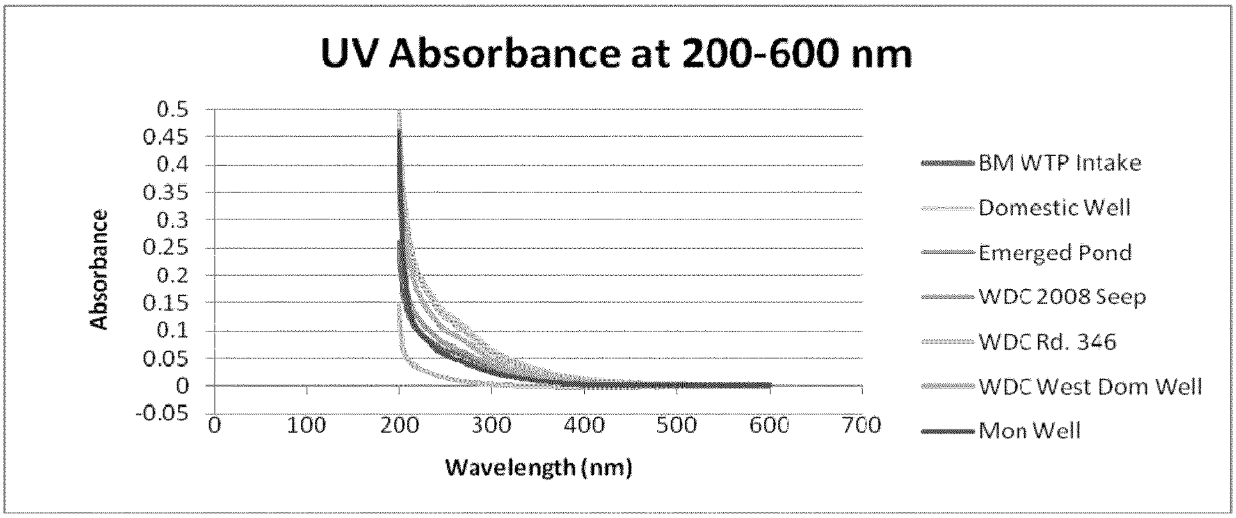

Figure seven: the ultraviolet absorbance for eight of the samples collected

The graph for the absorbance from 200-600 for all eight of the samples also illustrates a low $SUVA_{254}$ in EnCana Monitoring Well 23 compared to the others. Aside from the Water Treatment Plant, which was clearly successful in removing organic matter through its treatment processes, its curve falls lowest; indeed much lower than that of the other shallow groundwater well only 100 yards away. The curve here is shown in red to distinguish it from the others, shown in blue. Its relationship to the other samples indicates that the organic matter present was likely not from natural biogeochemical activity near the surface, but from other organic carbon sources.

Liquid Chromatography/Mass Spectrometry (LC/MS)

The majority of the results of the LC/MS analysis were fairly typical for surface and shallow groundwater. Samples taken from several points along Divide Creek, as well as those from the Battlement Mesa water treatment plant and domestic well, all indicated relatively normal concentrations of organic matter. This was demonstrated in the form of a standard curve on the chromatograph, in which hydrophilic compounds “fell out” followed by increasingly hydrophobic compounds as they are ionized. The curve in the center is often referred to as “natural organic matter” (also called “unresolved complex mixture”).

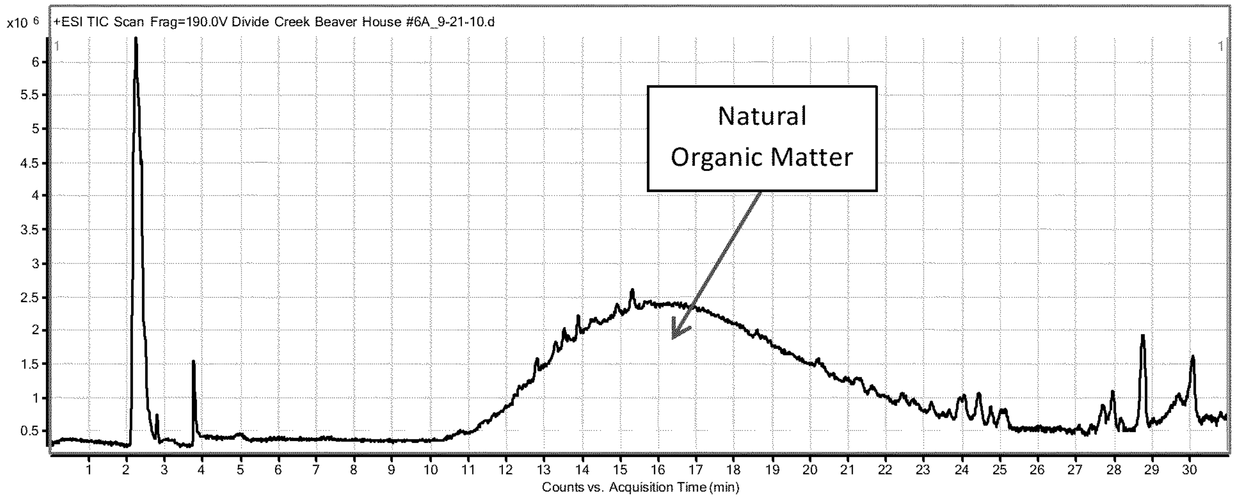

Figure eight: chromatograph for the Beaver House site along West Divide Creek.

This sample's chromatograph, taken from a point below the believed 2008 methane seep, shows what is typically indicative of surface water organic compound concentrations. The tall peak at the initial point along the graph, as well as the two very hydrophobic compounds towards the end, are compounds used in the sample preparation and concentration processes and are displayed in every chromatograph from the Center for Environmental Mass Spectrometry.

One sample, however, did indicate substantial quantities of a certain family of compounds. The sample taken from EnCana monitoring well #23 showed a set of five polyethylene glycols (PEGs): PEG-8, PEG-9, PEG-10, PEG-11, and PEG-12. Each of these is demonstrated by a different peak, shown below. For example, the first major peak is the lightest of the five compounds: PEG-8. The peak following it is PEG-9, the third is PEG-10, and so on. Diagnostic ions are defined as "a fragment ion found in all members of family of compounds, which is characteristic only of that family" (Ferrer and Thurman, 2003). They can be highly useful in identifying PEGs, specifically m/z 89, 133, and 177. In this case, these ions are formed by the fragmentation and cyclization of the ethylene glycol chain. The "Diagnostic Ion Approach," as it has been named, is particularly useful in LC/MS over other techniques of compound identification.

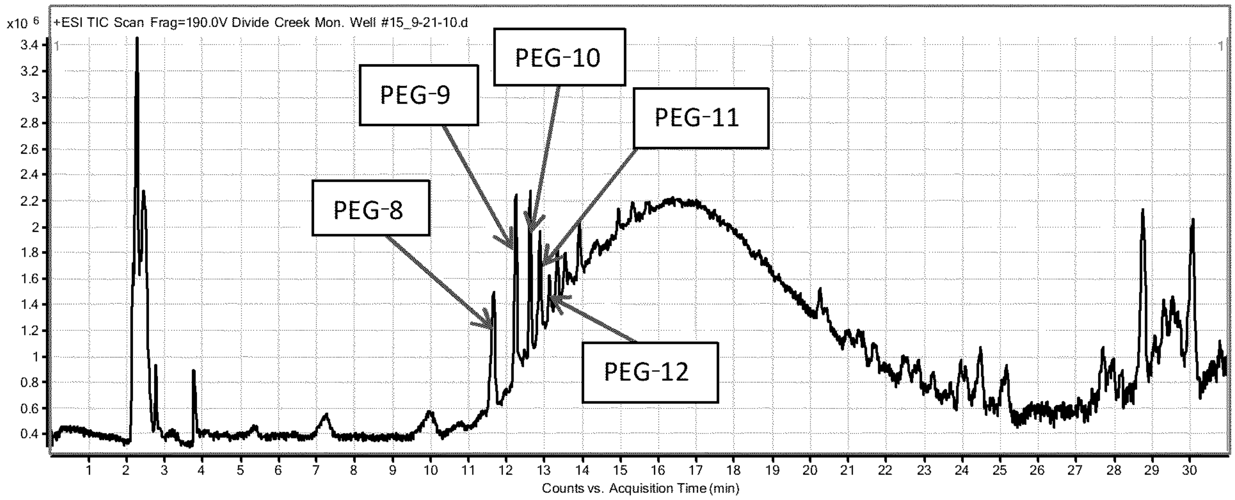

Figure Nine: Chromatograph of EnCana monitoring well 23, featuring a family of polyethylene glycols

In previous research on polyethylene glycols conducted by Profs. Mike Thurman and Imma Ferrer, the family of compounds was identified through several characteristics. First, they observed several sequential chromatographic peaks (much like those observed in the chromatograph for EnCana monitoring well 23) that were close in retention time and had apparently protonated molecules $[M+H]^+$ and that the atomic masses of each peak increased at an equal interval, in this case by 44 units. The same three ions also appeared in each of the chromatographic peaks, suggesting a homologous relationship between them.

Compounds were identified by extracting the molecular weight of each PEG compound and running it through the Agilent Technologies software. Upon determining a set of potential candidates, we were able to select the correct chemical formula based on statistical

MS Formula Results: + Scan (11.633 min)

m/z	Ion	Formula	Abundance
371.227	(M+H)+	C16 H35 O9	106333.6

Best	Ion Formula	Score	m/z	Calc m/z	Diff (ppm)	Mass Match
☑	C16 H35 O9	98.37	371.227	371.2276	1.53	98.08
☐	C13 H27 N10 O3	95.22	371.227	371.2262	-2.13	96.35
☐	C11 H32 N8 O4 P	94.96	371.227	371.2279	2.34	95.58

Figure ten: The possible chemical formula for several compounds corresponding to that molecular weight

probability. PEG-8 had an ion formula of C16H35O9, with a score of nearly 99%. We subtracted one hydrogen ion from each chemical formula, because this was the ion added at the start of analysis. This would indicate that PEG-8 has H34, PEG-9 had H38, etc.

Polyethylene glycol is a polymer of ethylene oxide and water. It consists of a number of ethylene groups ($H_2C=CH_2$) combined with an oxygen, hydrogen, and hydroxide group. In its pure form, it is characterized as a clear viscous liquid at a lower molecular weight; wax-like substance at a mid-range molecular weight; and as an opaque white crystalline solid at high molecular weights (chemindustry.ru). The *n* represents the number of ethylene and oxygen groups present: in the case of our results, it would be 8 through 12. It is also perfectly soluble in water, however, as the weight of the polymer increases solubility decreases.

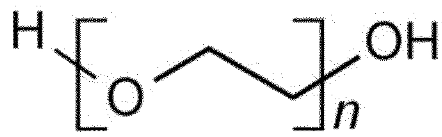

Figure eleven: the polyethylene glycol molecular formula

Hydraulic Conductivity and pH

Sample Name	pH	Conductivity (K) μscm^{-1}
Battlement Mesa WTP Outflow	6.59	92
Battlement Mesa WTP Intake	7.97	94
Divide Creek Beaver House	8.20	70
Divide Creek Emerged Pond	7.60	75
Divide Creek 2008 Seep	8.73	72
Divide Creek W of Dom Well	8.66	72
Domestic Well Spigot	7.05	81
COGCC Monitoring Well	7.13	129
Divide Creek Rd. 346 Bridge S	8.21	80

Table five: pH and Conductivity

The readings we found for conductivity (K) and pH did not demonstrate any alterations as a result of natural gas activity. We were relatively surprised to find that pH was fairly high at all sample sites taken from West Divide Creek, which could indicate the presence of a limestone deposit or other alkaline substrate. Conductivity, essentially a measure of the "saltiness" of a fluid, was fairly standard for surface water, and most values were in the same range. These measurements can vary widely, with ocean water reaching micro-Siemens in the 100,000s.

Discussion

Our results yielded little evidence of the presence of toxic compounds in West Divide Creek or Battlement Mesa Water treatment plant. However, this does not discount the fact that cases of contamination have been occurring in regions like Garfield County who are in the midst of natural gas activity. Many other studies have shown that toxic metals and metalloids, dangerous organic compounds, and elevated salinity are present in wastewaters from drilling and extraction; limitations of this study may have prevented them from being discovered had they been present in Garfield County previously or currently. This section will seek to explore what we did discover and its potential sources.

PEGs: Industrial Uses, Potential Toxicity, and Fate

The discovery of polyethylene glycols in EnCana monitoring well #23 near West Divide Creek could be attributed to several sources. There is a wide range of uses for the compound, which posses dispersing properties valuable for operations in a variety of industries. In its low molecular weight forms, it can be used in pesticide application (to enhance the spread of the product on plant surfaces), food waxes, as a plasticizer, in water soluble lubricant for rubber molds; wetting or softening agents, in the production of urethane rubber, and as components of detergents. In medicine, PEGS can be used as laxatives, ointments, ophthalmic solutions, and sustained release oral pharmaceuticals (Sheftel, 2000). It can also serve as a thickening agent in hydraulic operations, as a flocculating agent and coagulant in ore dressing processes and for sedimentation of dredges, as a binding agent and thickener for latex and paints, in separators and electrolyte solvents in lithium polymer cells as a polar stationary phase for gas chromatography, and as water-soluble film in food packaging (ChemIndustry.ru).

The potential may exist for these PEGs to come from natural gas activity, as they are used in drilling operations for oil and gas in some regions. In China, they utilize water-based

PEG drilling fluids that also contain polymers and inorganic salts. PEGs make favorable drilling fluids due to their shale inhibition, strong lubricating ability, and the ability to adjust flow-patterns (Ling, 2006). Polyethylene glycol ethers, also called methoxypolyethylene glycol and polyglymes, have been used for over 30 years as physical absorbents for acid gas and removal of sulfur-containing compounds from natural and synthetic gases (Henni, 2005). This was an important step as part of the Kyoto Protocol to reduce carbon dioxide emissions; a process deemed "gas sweetening."

Surfactants are sometimes used in fracking operations, as they are believed to cause easier flow of natural gas to the wellbore. If high levels of migration were occurring from a fractured formation, the possibility may exist for us to detect some concentrations of a solvent. However, our limited knowledge of the exact composition of fracking fluids made it impossible to determine if this set of PEG compounds came from that source; and there is no guarantee that EnCana, the company responsible for many of the wells in the area, has used PEGs in their natural gas drilling operations. In order for LC/MS to determine with high levels of accuracy if compounds present were from fracking fluid, a sample of the fluid would need to be obtained for a compound-by-compound comparison.

While a methane seep like the ones that occurred in 2004 and likely in 2008 could have caused migration of PEGs used in the drilling or fracturing process to surface and shallow groundwater, the probability is rather low. The TOC values we found in both shallow groundwater samples were mostly likely not due to unnatural sources of organic compounds, but to the high levels of mixing between ground and surface water that occur through the process of exchange in the hyporheic zone. This mixing could allow PEGs to be transported into the wells from numerous sources: an upstream neighbor could have washed his car and allowed soaps (solvents) to run into West Divide Creek. High surface-groundwater exchange rates also reduces the possibility of these compounds coming from deep within a formation and remaining there for several years.

Despite our uncertainty about the exact source of these PEGs, we can conclusively state that they are manmade and not from natural causes. Due to our knowledge of their use in drilling processes, it seems probable that PEGs could have been used as a lubricant or other fluid thickener in the process of drilling EnCana monitoring well #23. PEGs of varying molecular weights may persist for several years in water depending on microbial activity, so it would be possible for constituents used in the 2008 drilling of the well to remain present at the time of our sample collection. It is as of yet unconfirmed if EnCana used PEGs in their drilling processes.

The discovery of PEGs in shallow groundwater is indeed no cause for concern for those using it for residential or any other purposes. They are considered to be inert and possess a very low order of toxicity to humans (Sheftel, 2000). Their use in pharmaceuticals, soaps, and food additives indicates that they are generally safe for human consumption. Its Material Safety Data Sheet stated that there are essentially no adverse health effects from inhalation, skin or eye contact, although ingestion of large doses of lower-molecular weight products may cause an upset stomach (just as some of us have observed after accidentally ingesting household soaps). Its toxicity is so low that the EPA did not even feel it was necessary to list it in their Integrated Risk Information System (IRIS).

Study Limitations

Our examination of the impacts of natural gas activity to water quality in Garfield County was limited by several factors that may have prevented us from finding potential contaminants. For example, the preliminary nature of the study only allowed for sample collection over a period of a day. Studies with a greater abundance of resources, both financially and temporally, would have taken more samples from a broader range of locations over a sustained period of time. This would account for changes in stream-flows and relationship to drilling and fracking operations. Attempting to take samples from surface water can be highly variable- they merely provide a "snapshot" of the time in which the sample is taken and may not be indicative of overall water quality.

Analysis methods could also have limited our findings. LC/MS is extremely accurate in analyzing compounds of a particular nature, typically those that are of heavier molecular weights and ionize easily. However, many of the compounds we identified in previous water quality studies and government reports had a low molecular weight, often less than 100 g/mol. This typically means that they readily volatilize (indeed, many of them are identified as *volatile* organic compounds) and could even have escaped during sample preparation. The BTEX compounds are of a low molecular weight and do not ionize largely due to their heterocyclic nature; yet they remain one of the greatest concerns related water contamination from natural gas activity. Commonly used fracking fluid constituents like gluteraldehyde and polyacrylamide are also of too light a molecular weight to be identified by LC/MS. To more comprehensively study these compounds, use of GC/MS is recommended.

Industry Best Practices and Policy Recommendations

Improving technology

The technology involved in natural gas extraction has made huge leaps in the last few decades, improving the efficiency and in many cases reducing the environmental impacts of natural gas activity. While directional drilling, produced water recycling, and pipelines are all a step in the right direction, the potential exists for many companies to further improve their practices. Reduction in the use of toxic chemicals or conversion to non-toxic ones in the drilling and fracking process can be just as efficient and far less harmful. Evidence suggests that wells fractured with simply water and proppant are just as efficient at production if not more so than those fractured with a gel-based solution that can contain hundreds of toxic chemicals (Mall, 2007).

Closed-loop and closed-containment systems, which many companies have already begun to utilize, can vastly decrease the amount of waste released into water supplies and reduce the freshwater necessary for drilling and extraction processes. Use of closed water tanks (meaning that they are sealed on top), instead of open pits vastly decreases the potential for wastewaters to seep into soil and enter underground drinking water supplies as well as emit toxic volatile organic compounds. To make their use as effective as possible, above-and-below ground tanks should both have multiple layers of containment and leak detection; this is essential because tanks, particularly those containing acidic compounds like those found in wastewaters, can cause corrosion over time. These tanks are also more effective than pits because they can be moved from a site after the well stops producing. They require less earthmoving, which in turn requires less backfilling and disposal of contaminated liners (earthworksaction.org).

Many companies are beginning to discover that technologies that allow them to capture excess gasses from within the well can be more economical while reducing toxic volatile organic compounds that are believed to be causing ill health effects. Some studies have shown that "each volume of gas not vented into the atmosphere is a volume of gas sold" (Mall, 2007). While sometimes the companies do not actually make a profit from implementing vapor recovery units and similar technologies, they typically cover their costs. Williams Production Company recently realized they can make up to 10 dollars for every dollar invested on their recovery technologies.

The EPA's Natural Gas STAR program "encourages oil and natural gas companies to adopt proven, cost-effective technologies and practices that improve operational efficiency and reduce methane emissions" (epa.gov/gasstar). Because methane is one of the most potent greenhouse gases, reducing its emissions from natural gas operations can be tremendously beneficial to the environment. There are numerous points throughout the journey of natural gas where these methane (and other more toxic) emissions could occur. The EPA has listed best practices for the industry to use in their compressors/engines, dehydrators, pneumatics/controls, pipelines, tanks, valves, and wells. Implementation can pay off between one year and over ten years depending on the process. Technologies like "green completion" involve bringing equipment on site to clean up produced gas as it is initially being brought to the surface; the EPA also recommends installing velocity tubing strings, down-hole separator pumps, and compressors to capture casing-head gas.

Policy recommendations

There are several policy changes that many believe could alter the political landscape surrounding natural gas, and in turn improve its safety. Currently, a bill is waiting for review that has the potential to change entirely the way the industry is regulated. Named the Fracturing Responsibility and Awareness of Chemicals Act, it contains provisions that would require natural gas companies to release the composition of their fracking fluid to both regulatory agencies and medical professionals. It then goes on to say that "the state (or the administrator, as applicable) shall make available to the public the information contained in each disclosure of chemical constituents… including by posting the information on an appropriate website." This would hopefully give the EPA and other agencies such as the state the authority to monitor and control the use of fracking fluid.

Some states have decided they were unwilling to wait for this bill to be passed or for the EPA to conduct its proposed study. Wyoming is now the first state in the nation to declare that natural gas companies must make public the ingredients used in their fracking fluids. In June of this year (2010) the Wyoming Oil and Gas Conservation Commission unanimously ruled that ingredients would be reported at the insistence of Governor Dave Freudenthal. According to ProPublica, the nonprofit journalism outfit that has been looking into the effects of fracking over the last few years, as much as 85 percent of the fracking fluids are left underground after wells are drilled (NewWest.com, 2010).

Wyoming used the information found in this study as impetus for their new regulations. Several energy companies with a presence in the state have responded with opposition to these regulations, and none of them as strongly as Halliburton, the leading developer of hydraulic fracturing technology. However, the state remains firm in their legislation: "Halliburton sent a big-time lawyer to talk to us, but it didn't go well for him," said Freudenthal. This legislation, in conjecture with the Fracturing Responsibility and Awareness of Chemicals Act, may open the door for other states affected by the natural gas industry to enact the same policies.

Other policy improvements would include placing natural gas activities under the supervision of CERCLA: the Comprehensive Environmental Response, Compensation, and Liability Act. This act covers the release or potential threat of release of hazardous substances into the environment. It holds the company responsible for the spill accountable; and, in the event that they cannot pay for cleanup, it oversees the use of the superfund for remediation. Many of the synthetic chemicals used in drilling and extraction processes are regulated under CERCLA, but when a release of naturally occurring contaminants such as POHs occurs, there is little funding or enforcement available. If these exemptions were removed, companies would be held responsible for cleanup of oil and gas spills where they are released into the environment and pose a threat to human health. (Mall, 2007).

Conclusion

Our study could make no real case for natural gas activity seriously impacting water quality in Garfield County. However, studies like those conducted on the Mamm Creek Field and in 2004 on the Divide Creek seep have provided strong evidence for contamination. Residents in areas like Pavillion, WY, and Dimock, NY are almost certainly being affected by natural gas activity. While companies drilling and fracking in these areas assert that they are not responsible for these impacts, it seems highly unlikely that the presence of hydrocarbons in domestic wells could be attributed to other sources. These cases of contamination indicate the need for improved operational practices and technology as well as stronger regulatory power over fracking and drilling fluid use.

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